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Research review paper

Bioimprinting strategies: From soft lithography to biomimetic sensors and beyond ☆

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ABSTRACT

Imprinting is a straightforward, yet a reliable technique to develop dynamic artificial recognition materials—so called as synthetic antibodies. Surface imprinting strategies such as soft lithography allow biological stereotyping of polymers and sol–gel phases to prepare extremely selective receptor layers, which can be combined with suitable transducer systems to develop high performance biomimetic sensors. This article presents an overview of the remarkable technical advancements in the field of surface bioimprinting with particular emphasis on surface imprinted bioanalyte detection systems and their applications in rapid bioanalysis and biotechnology. Herein, we discuss a variety of surface imprinting strategies including soft lithography, template immobilization, grafting, emulsion polymerization, and others along with their biomimetic sensor applications, merits and demerits. The pioneering research works on surface patterned biosensors are described with selected examples of detecting biological agents ranging from small biomolecules and proteins to living cells and microorganisms.

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☆ Dedicated to Prof. Franz L. Dickert on the occasion of his 70th birthday.

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1. Introduction

One of the major concerns in the design of modern biosensors (Ferreira et al., 2009; Sassolas et al., 2012; Tothill, 2009) is the selection of suitable receptor material that possesses comparable selectivity to that of natural receptors (or antibodies) and that can work effectively under different conditions (Groves et al., 1998; Wolff et al., 2001). Undoubtedly, natural antibodies are exceptionally selective and fast responsive in bio-molecular recognition. However, their tedious derivation, instability in complex matrices, and regeneration problems are the main downsides, which trigger the quest for synthetic antibodies (Baggiani et al., 2008). These synthetic antibodies overcome such problems and often exhibit satisfactory selectivity.

Molecular imprinting (Mosbach, 1994; Mosbach and Ramstrom, 1996) is among the most widely studied techniques during the last decade for crafting biomimetic sensor layers. Since these materials are not only capable of withstanding in complex matrices under tough conditions, they also demonstrate receptive characteristics as good as natural antibodies. Molecularly imprinted polymers (MIPs) have a broad range of applications as they can be tuned for recognizing a large variety analytes ranging from nanoscale molecular analytes (Lieberzeit et al., 2007a; Pardieu et al., 2009) to sub-micrometer bio-species (Dickert et al., 2003).

In the first case, i.e. to detect small molecules, bulk imprinting (Brüggemann et al., 2000) is generally preferred to generate readily accessible and template-specific interaction sites within the chemoselective material that could either be a whole polymer matrix (Lieberzeit et al., 2008) or inorganic nanoparticles (Lieberzeit et al., 2007b) or both, i.e. nanocomposites. The inclusion and release of desired molecular analytes are generally faster and fully reversible, which ensure the use of bulk-imprinted synthetic antibodies for several rounds of analyses both in liquid (solution) as well as in gaseous states. Therefore, bulk imprinted materials have been considered highly useful for sensing molecular or even ionic analytes (Latif et al., 2011; Rao et al., 2006).

However, bulk-imprinting strategies found some distinct limitations in case of larger, micro-sized bioanalytes such as living cells and microorganisms. This is due to the fact that the diffusion rates of bioanalytes are slow leading to much longer response time and drift problems. Moreover, the release of incorporated analytes from imprint centers is not completely achieved, which gradually leads to poor regeneration. These complications have been overcome by an innovative imprinting technique that is known as surface imprinting (Hayden and Dickert, 2001; Yoshida et al., 2000).

Surface imprinting yields selective sensing layers in which the recognition of macromolecular or bioanalytes is exclusively carried out at the surface of a polymeric or a sol–gel material. Herein, the polymer surface is crafted in such a fashion that it acquires both the geometrical and chemical fit (imprint) of the target analyte (Jenik et al., 2009a), consequently delivering highly specific recognition events. The transfer of analyte to and from the sensor surface takes place in a straightforward way, thus achieving significant reversibility and fast response and recovery times. Surface imprinted polymers and nanomaterials have been widely explored for different types of analytes ranging from microorganism and cells (Lieberzeit et al., 2005a; Mujahid and Dickert, 2012) to proteins and molecular analytes (Ge and Turner, 2008; Li et al., 2013; Lv et al., 2013).

In sensor design, surface imprinted layers may exhibit lower sensitivity as compared to bulk imprinted materials due to reduced number of structurally adapted affinity centers. Nonetheless, surface imprinting technique offers several advantages over other synthetic methodologies to prepare selective recognition layers for bio-analytes. One of the major benefits of surface imprinting is that apart from typically micro- or macro-scale bioanalytes, this technology possesses equally good potential for nano-scale molecular targets, e.g. herbicides (Xu et al., 2011). Therefore, surface imprinting has found useful applications in various forms of bio-recognition phenomena.

Over the years, a number of different procedures have been developed for surface imprinting of polymeric layers, nanobeads, and inorganic nanoparticles. In general, the nature of template and/or target analyte is decisive in devising techniques for the fabrication of surface imprinted materials. For instance, soft lithography (Kane et al., 1999) is a promising tool for fabricating recognition layers for living cells and microorganisms (Hayden et al., 2003), but proteins (Bossi et al., 2007) and other macromolecules can be suitably imprinted by e.g. adapting the idea of immobilized templates on sacrificial supports. In addition to the imprinting strategy, the synthetic route also plays an important role in developing precise interaction sites for specific rebinding of the target (Hillberg and Tabrizian, 2008).

This review article is focused on the selected surface imprinting strategies, which have been primarily developed for biomimetic sensing applications. The state-of-the-art biomimetic sensors for detection of living cells, microorganisms, proteins and other macromolecules are discussed along with their relative merits and demerits. The most recent developments in the surface imprinting techniques are highlighted to reveal their potential in imparting specific recognition features to different types of materials. Moreover, some innovative examples of surface imprinted bio-mimetic sensors are discussed to represent recent trends in this field.

2. Soft lithography: a soft approach to surface patterning

Soft lithography (Whitesides et al., 2001; Xia and Whitesides, 1998) or stamping technique for synthesis and fabrication of surface imprinted materials has emerged as a magnificent tool in the development of selective biomimetic sensors. It is a non-photolithographic strategy first introduced by Bain and Whitesides (1989) for micro- and nanoscale patterning. It is a convenient and effective method for micro- and nano-fabrication based on self-assembly and replica molding. Soft lithography does not require expensive materials or specialized equipment. It uses a soft polymeric stamp to imprint a solution of molecules or bio-species onto a solid substrate and to generate surface patterns with feature sizes ranging from 30 nm to 100 μm (Whitesides et al., 2001).

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